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(56) Documents Cited
GB 2223188 A GB 2222785 A GB 2219223 A
GB 2195560 A GB 1441684 A
Abstracts of JP 05106057 A (Nisshin Steel Co. Ltd.)

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UK CL (Edition) B2E
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Online databases: EDOC, JAPIO, WPI

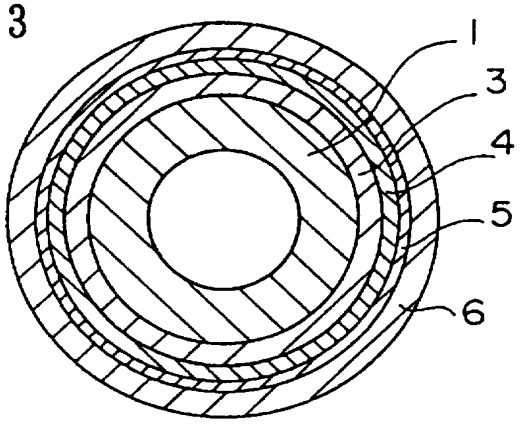
(54) Corrosion-resistant fluororesin coatings for tubes

(57) The present invention provides a corrosion resistant resin coating structure excellent in corrosion resistance, weather resistance and chemical resistance, mechanically tough and strong and having high heat resistance temperature.

A steel tube 1 optionally having a copper layer is formed. Then, a zinc or zinc/nickel plating layer 3 is formed on the outer circumferential surface of the steel tube, and a chromate film 4 comprising a trivalent chromium compound is formed on the zinc or zinc/nickel plating layer. At least one layer of polyvinyl fluoride or polyvinylidene fluoride layer 6 is formed, as required, by way of an epoxy resin intermediate layer 5. A sufficiently satisfactory results are obtained in corrosion resistance test.

They are used as pipelines for automobiles or feeding oil and air to various kinds of machinery.

Fig. 3



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At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

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Fig. 1

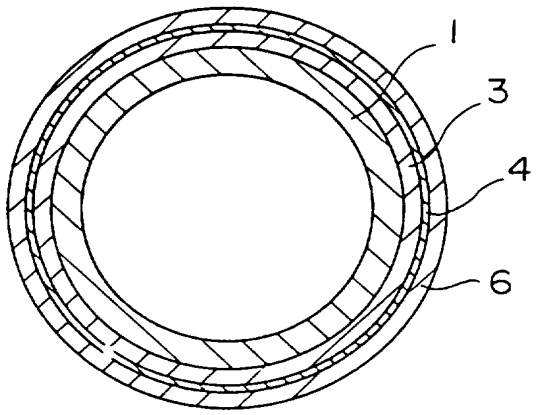

Fig. 2

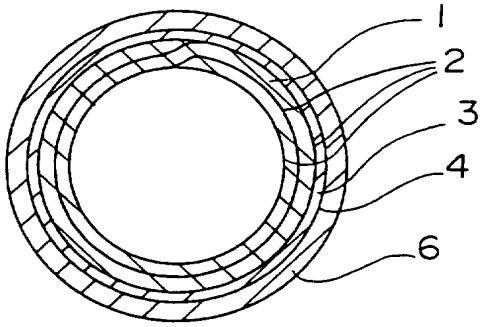

Fig. 3

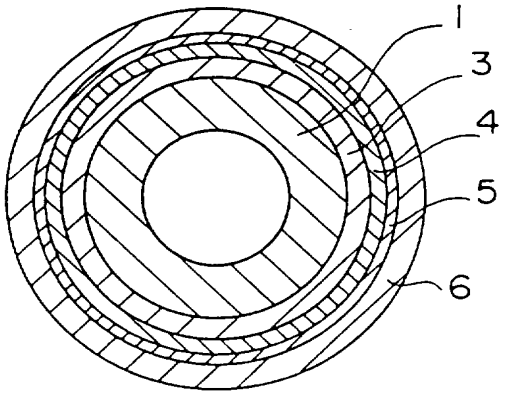

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Fig. 4

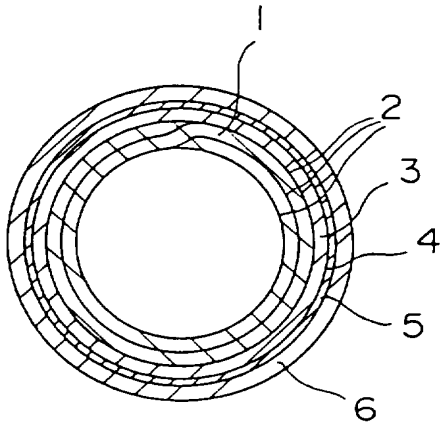
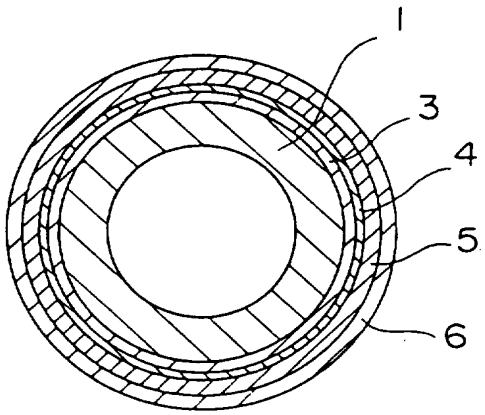


Fig. 5



CORROSION RESISTANT RESIN COATING STRUCTURE IN A METAL TUBE

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention concerns a corrosion resistant resin coating structure in a metal tube, in particular, a metal tube of a tube diameter, particularly, of less than 30 nm, having excellent adhesion and excellent chemical and mechanical corrosion resistance, which is disposed in plurality as pipelines for brake oil or fuel of automobiles or feed channels for feeding oil or air to various kinds of machines and equipments.

Description of the Prior Art

A protection coating has been applied to an outer surface of a metal tube. For instance, pipelines for brake oil or fuel of automobiles undergo severe working conditions since they are disposed to an under floor surface of the automobiles, and they are required to have chemical resistance, as well as scratch resistance, impact resistance or resistance to injuries caused by external mechanical forces. Further, corrosion of pipelines caused by rock salt as a road anti-freezing agent has presented a

further problem. Accordingly, it has been desired to have a metal tube structure applied with a protection coating capable of withstanding mechanical erosion and also chemical corrosion, for which various proposals have bee made.

There have been known protection coatings, for example, formed by applying a zinc plating layer by electric plating on an outer surface of a metal tube, forming a relatively thick olive-colored specific chromate film on the plating layer and forming a fluoro resin layer further thereon (for example, in Japanese Patent Publication Sho 57-60434 and Sho 61-23271), forming a polyvinyl fluoride layer comprising two fluoro resin layers fused to each other (Japanese Utility Model Publication Hei 3-11517) and, further, forming an epoxy resin intermediate layer between a chromate film and a polyvinyl fluoride layer (Japanese Patent Application Sho 62-84429).

In such known corrosion resistant resin coating structures in metal tubes, an epoxy resin intermediate layer or a fluoro resin such as a polyvinyl fluoride resin is coated by way of a relatively thick chromate film formed from a chromate solution comprising hexavelant chromium ions on a zinc plating layer applied at least to an outer circumferential surface of a tube material. However, since the resin layers are baked at high temperature, it results in a problem that the chromate film suffers from

remarkable thermal degradation and the corrosion resistance inherent to the chromate film is inevitably reduced by the heat treatment. Further, formation of the chromate film with a chromate solution generally involves a problem that hexavalent chromium ions contained in a treating solution and an acid added as a reducing agent are consumed in a great amount, so that each of ingredients of the treating solution has to be supplemented and renewed at a predetermined interval for maintaining a certain layer-forming performance, which increases a cost for disposing wastes containing a great amount of deleterious hexavalent chromium. Further, although the chromate film as formed by the chromate solution is of a large layer thickness and has excellent corrosion resistance, water content is expelled by heat applied when the resin layer is formed to make the coating film brittle, which leads to fine cracks by plastic deformation caused by subsequent bending fabrication or flare fabrication at tube ends, to bring about a problem of reducing the inherent anti-rust performance.

SUMMARY OF THE INVENTION

It is, accordingly, an object of the present invention to provide a corrosion resistant resin coating structure of excellent corrosion resistance, weather resistance and chemical resistance, having mechanical strength and tough

and having a high heat resistant temperature.

The present inventor has made various studies for solving the foregoing problems and attaining the above-mentioned object and, as a result, has accomplished the present invention based, in particular, on the finding that the above-mentioned object can be attained by forming a chromate film by using a chromate solution containing only trivalent chromium ions.

This is, the present invention provides a corrosion resistant resin coating structure of a metal tube comprising a metal tube, a zinc or zinc/nickel plating layer formed on an outer circumferential surface of the metal tube, a chromate film comprising a trivalent chromium compound formed on the plating layer and a polyvinyl fluoride layer or a polyvinylidene fluoride layer formed on the chromate film. The present invention further provides a corrosion resistant resin coating structure comprising a thin-walled fine diameter metal tube, a zinc or zinc/nickel plating layer formed on an outer circumferential surface of the thin-walled fine diameter metal tube, a chromate film comprising a trivalent chromium compound formed on the plating layer, an epoxy resin intermediate layer formed on the chromate film and a polyvinyl fluoride layer or a polyvinylidene fluoride layer formed by way of the intermediate layer.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross sectional view of a preferred embodiment of a corrosion resistant resin coating structure corresponding to Example 1 according to the present invention, exaggerated in a diametrical cross section of a metal tube;

Fig. 2 is a cross sectional view of a preferred embodiment of a corrosion resistant resin coating structure corresponding to Example 2 according to the present invention exaggerated in a diametrical cross section of a metal tube;

Fig. 3 is a cross sectional view of a preferred embodiment of a corrosion resistant resin coating structure corresponding to Example 3 according to the present invention exaggerated in a diametrical cross section of a metal tube;

Fig. 4 is a cross sectional view of a preferred embodiment of a corrosion resistant resin coating structure corresponding to Example 4 according to the present invention exaggerated in a diametrical cross section of a metal tube; and

Fig. 5 is a cross sectional view of a metal tube of the prior art, exaggerated in a diametrical cross section.

DETAILED DESCRIPTION OF THE INVENTION

As a metal tube in the present invention, a single-wound steel tube or a double-wound steel tube prepared from a SPCC steel sheet is used for instance and the tube may have a copper plating layer of about 3 um thickness to an outer circumferential surface. Further, as a steel tube, electrounite steel tube or drawn steel tube may also be used and, further, other metal tubes of appropriate material such as an aluminum tube or a steel tube may also be used. In addition, there is no particular restriction on the wall thickness of the metal tube and both thin-walled and thick-walled tube may be used.

The zinc plating layer is formed by using a generally known alkali electrolyzing solution containing an electrolyzing solution rendered acidic with sulfuric acid or zinc cyanate, and the zinc/nickel plating layer is formed by an electrolyzing solution rendered acidic with hydrochloric acid.

For the chromate film, a chromate treating solution at a low concentration of trivalent chromium ion conc (1 g)/l is used to form a blue white chromate film.

In the present invention, since the chromate film is formed by using a chromate solution only containing trivalent chromium ions, it can remarkably reduce heat degradation at a high temperature upon heat drying after coating

the epoxy resin and the fluoro resin and, at the same time, it provides excellent close adhesion with the epoxy resin intermediate layer. It is considered that since the chromate film formed from the chromate solution containing trivalent chromium ions comprises a trivalent chromium complex compound and forms a relatively thin passivated layer, it suffers from less heat degradation. Further, although it has been found that the trivalent chromium complex compound layer has excellent close adhesion with the epoxy resin layer, details for the mechanism are not apparent.

The epoxy resin intermediate layer is formed, for example, by using epoxy-polyester and applying heat treatment at 250°C for 60 sec.

Examples of the present invention will be explained with reference to the appended drawings.

Example 1

(1) Metal tube: Single-wound steel tube 1 having 4.76 mm outer diameter and 0.7 mm wall thickness was fabricated from a CC steel sheet.

(2) Zinc plating layer: A zinc plating layer 3 of 25 um thickness was formed on an outer circumferential surface of the single-wound steel tube 1 fabricated using zinc sulfate as a main ingredient, adding an organic additive

and supplying an electric current at a current density of 60 A/dm^2 at a temperature from 55 to 60°C.

(3) Chromate film comprising a trivalent chromium compound: A blue white chromate film 4 was formed on the zinc plating layer 3 obtained in (2), by a low concentration chromate treating solution at trivalent chromium ion conc (1 g)/l.

(4) Fluoro resin layer: A polyvinyl fluoride layer 6 of 20 um thickness was formed by dipping the single-wound steel tube 1 subjected to the treatment (2), (3) above into a solution containing polyvinyl fluoride dispersed in diethyl phthalate, thereby to applying coating, and applying heat treatment at 300°C for 60 sec.

(5) Corrosion resistance test: For five products manufactured as described above, test pieces were cut each into 300 mm to prepare ten test specimens in total. Then, injuries leaching the substrate steel were made each at 20 mm interval and a salt spray test according to JIS Z 2371 was conducted for 1,000 hours for the portions while leaving one-half of the test specimens as they were and heating another half of the test specimens at 150°C for 24 hours. Subsequently, a cellophane tape was closely bonded to and peeled from the knife injured portions to measure the maximum peeling width of the fluoro resin layer from the knife injured portion. The results are shown in Table 1.

Example 2

(1) Metal tube: Double-wound steel tube 1 having 8 mm outer diameter and 0.7 mm wall thickness was fabricated from a SPCC steel sheet having a copper layer 2 of 5 um film thickness.

(2) A zinc plating layer 3, (3) chromate film 4 comprising a trivalent chromium compound were formed by the same manner as in Examples 1-(2) and (3). (4) Fluoro resin layer: A polyvinyl fluoride layer 6 of 20 um thickness was formed by dipping the single-wound steel tube 1 subjected to the treatment (2), (3) above into a solution containing polyvinyl fluoride dispersed in diethyl phthalate to apply coating, and applying heat treatment at 300^{o}C for 60 sec.

(5) Corrosion resistance test was conducted in the same manner as in Example 1-(1). The results are shown in Table 1.

Comparative Example 1

Corrosion resistant resin coating tubes were manufactured in the same manner as in Example 1 except for using a chromate solution containing hexavalent chromium ions for chromate films, and a corrosion resistance test was conducted in the same manner as in Example 1-(5), and the results are shown in Table 1.

Table 1

(Unit: mm)

	Example 1		Example 2		Comp. Example1	
	Not-heated	Heated	Not-heated	Heated	Not-heated	Heated
1	7	6	6	7	9	12
2	6	10	8	8	11	14
3	9	8	5	7	10	13
4	8	8	6	8	13	16
5	6	7	6	6	10	15
Average	7.2	7.8	6.2	7.4	10.6	14.0

Example 3

(1) Metal tube: Electrounite tube 1 having the same material as in Example 1-(1) and having 6.35 mm outer diameter and 1.5 mm wall thickness was used.

(2) Zinc plating layer 3, (3) chromate film 4 comprising trivalent chromium compound was formed in the same manner as in Examples 1-(2), (3).

(4) Epoxy resin intermediate layer: Epoxy resin intermediate layer 5 was dipped, for example, by using epoxy-polyester and coated, heat treatment was applied at 250°C for 90 sec to form an epoxy resin intermediate layer of 5 um thickness was formed by dipping, coating and heat treating at 250°C to 90 sec to form epoxy resin intermediate layer of 5 um film ester by heat treatment at 90°C for 250°C.

(5) Fluoro resin layer: A polyvinyl fluoride layer 6 is shown in the same manner as in Example 1-(4).

(6) Corrosion resistance test: It was conducted in the same manner as in Example 1-(1), and the results are shown in Table 2.

Example 4

(1) Metal tube: Double-wound steel tube 1 as in Example 1-(1) was used.

(2) Zinc plating layer 3, (3) chromate film 4 comprising

trivalent chromium compound was formed in the same manner as in Examples 1-(2), (3).

(4) Epoxy resin intermediate layer: Epoxy resin intermediate layer 5 was formed in the same manner as in Example 3-(4).

(5) Fluoro resin layer: A polyvinyl fluoride layer 6 is shown in the same manner as in Example 2-(4).

(6) Corrosion resistance test: It was conducted in the same manner as in Example 1-(1), and the results are shown in Table 2.

Comparative Example 2

Corrosion resistant resin coating tubes were manufactured in the same manner as in Example 3 except for using a chromate solution containing hexavalent chromium ions for chromate films, and a corrosion resistance test was conducted in the same manner as in Example 1-(5), and the results are shown in Table 2.

Table 2

(Unit: mm)

	Example 3		Example 4		Comp. Example 2	
	Not-heated	Heated	Not-heated	Heated	Not-heated	Heated
1	1	1	3	5	3	5
2	2	3	4	5	4	6
3	2	2	2	3	3	5
4	1	2	2	3	5	6
5	2	3	2	2	3	5
Average	1.6	2.2	2.6	3.6	3.6	5.4

As has been described above according to the present invention, since the chromate film was formed and constituted as described above by using a solution containing only trivalent chromium ions as the chromate solution, the film does not cause cracking or peeling also upon plastic deformation such as bending fabrication, as well as it is mechanically tough and strong, has high heat resistance temperature and is excellent in corrosion resistance, weather resistance and chemical resistance, to provide a remarkable effect.

WHAT IS CLAIMED IS

1. A metal tube and corrosion resistant resin coating structure in the metal tube having a first layer comprising zinc or zinc/nickel plating formed on an outer circumferential surface of the metal tube and a second layer comprising a chromate film composed of a trivalent chromium compound formed on the first layer and polyvinyl fluoride or polyvinylidene fluoride formed on the chromate film.

2. A corrosion resistant resin coating structure in a metal tube as defined in claim 1, wherein an epoxy resin intermediate layer is further interposed between the chromate film and the second layer.

3. A corrosion resistant resin coating structure in a metal tube as defined in claim 1 or 2, wherein a copper layer is further provided at the surface of the metal tube.

4. A corrosion resistant resin coating structure in a metal tube as defined in claim 1, 2 or 3, wherein the metal tube is a steel tube or an aluminum tube.

5. A corrosion resistant resin coating structure in a metal tube as defined in any of claims 1 to 4, wherein the metal tube comprises a single-wound tube, a double-wound tube, an electrounite steel tube or a drawn steel tube.

6. A metal tube and corrosion resistant resin coating

structure in the metal tube having a metal tube, a first layer comprising zinc or zinc/nickel plating formed on an outer circumferential surface of the metal tube, and a second layer comprising a chromate film composed of a trivalent chromium compound formed on the first layer, an epoxy resin intermediate layer formed on the chromate film, and polyvinyl fluoride or polyvinylidene fluoride formed as an intermediate layer.

7. A corrosion resistant resin coating structure in a metal tube as defined in claim 6, wherein the epoxy resin intermediate layer comprises epoxy-polyester.

8. A corrosion resistant resin coating structure in a metal tube as defined in claim 6 or claim 7, wherein a copper layer is further provided at the surface of the metal tube.

9. A corrosion resistant resin coating structure in a metal tube as defined in any of claims 6 to 8, wherein the metal tube is a steel tube or an aluminum tube.

10. A corrosion resistant resin coating structure in a metal tube as defined in any of claims 6 to 9, wherein the metal tube comprises a single-wound tube, a double-wound tube, an electrounite steel tube or a drawn steel tube.

11. A metal tube and corrosion resistant resin coating structure in the metal tube substantially as hereinbefore

described with reference to the Figures.

12. A corrosion resistant resin coating structure substantially as hereinbefore described with reference to the Figures.

The Patent Office

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Application No: GB 9517606.1
Claims searched: 1-12

Examiner: Diane Davies
Date of search: 21 November 1995

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.N): B2E

Int Cl (Ed.6): B32B 1/08, 27/30; F16L 58/04, 58/08, 58/10

Other: Online databases: EDOC, JAPIO, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
A	GB 2223188 A	(Usui Kokusai Sangyo KK) Whole document: Anticorrosion coating for metal pipes comprises zinc coat, chromate coat, and fluororesin layer.	
X,Y	GB 2222785 A	(Usui Kokusai Sangyo KK) Whole document: Anticorrosion coating for metal pipes comprises Zn/Ni coat, an optional chromate coat (see in particular, page 5 line 24), epoxy resin layer and PVF layer.	1-12
A	GB 2219223 A	(Usui Kokusai Sangyo KK) Whole document: Anticorrosion coating for metal pipes comprises zinc coat, chromate coat, epoxy resin layer and PVF layer.	
Y	GB 2195560 A	(Nippon Kokan KK) Whole document: anti-corrosion coating containing trivalent chromium and an epoxy resin layer.	1-12

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

The Patent Office

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Application No: GB 9517606.1 **Examiner:** Diane Davies
Claims searched: 1-12 **Date of search:** 21 November 1995

Category	Identity of document and relevant passage	Relevant to claims
X	GB 1441684 A (Usui Banditubing KK) Whole document: Anti-corrosion coating comprises zinc coating, chromate layer using chromic acid giving trivalent chromium (see page 2 line 45) and a PVF layer.	1-12
Y	Abstracts of JP 05106057 A (Nisshin Steel Co. Ltd.) A coating for stainless steel comprises a coating containing trivalent chromium ions and a fluororesin coating.	1-12

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.